

Potential Agronomic Benefits and Carbon Sequestration Ability of Biochar: Review

¹Bayu Dume and ²Amsalu Nebiyu

¹Department of Natural Resource Management,
College of Agriculture and Veterinary Medicine Jimma University, Jimma, Ethiopia

²Department of Horticulture and Plant Sciences,
College of Agriculture and Veterinary Medicine Jimma University, Jimma, Ethiopia

Abstract: Due to its aromatic structure, biochar is highly stable form of carbon in the soil that contributes to improve physicochemical and biological properties of soil and increased productivity due to the improvement of soil attributes and nutrient-use efficiency. Biochar can also play a great role to mitigate greenhouse gas emissions, like CO₂, N₂O and CH₄. This paper is briefly reviewed and synthesized recent findings and discussions regarding the agronomic benefits of biochar and its effects on global climate change and particularly in relation to the agricultural environmental effect of biochar in soil. Therefore, suitable experimental trials combining biochar types and different pedoclimatic conditions are needed to determine the extent to which these reactions influence the potential of biochar as a soil amendment, crop responses for increasing yield and instrument for carbon sequestration.

Key words: Biochar • Climate change • Carbon sequestration

INTRODUCTION

Plants obtain their nutrition from organic matter and minerals found in soils. As the land is farmed, the agricultural process disturbs the natural soil systems including nutrient cycling and the release and uptake of nutrients [1]. Modern agriculture is appropriate to mine the soil for nutrients and to reduce soil organic matter levels through repetitive harvesting of crops. This decline of the soil continues until management practices are improved, additional nutrients are applied, rotation with nitrogen-fixing crops is practiced, or until a fallow period occurs allowing a gradual recovery of the soil through natural ecological development. As the natural stores of the most important nutrients for plant growth decline in the soil, growth rates of crops are inhibited. The most extensive solution to this depletion is the application of soil amendments in the form of fertilizers containing the three major nutrients nitrogen (N), phosphorus (P) and potassium (K). Inorganic or commercial fertilizers have been the primary soil amendment since the dawn of the industrial age. Nitrogen fertilizers are often made using the Haber-Bosch process utilizing natural gas (CH₄) for the hydrogen and nitrogen gas (N₂) from the air to form ammonia (NH₃) as the end product. This ammonia is used

as a feedstock for nitrogen fertilizers, such as anhydrous ammonium nitrate (NH₄NO₃) and urea (CO(NH₂)₂). However, the use of these fertilizers contributes to greenhouse gas emissions, while similarly encouraging the depletion of the natural nutrient and minerals in healthy soils [2].

Biochar, the solid material obtained from the carbonization of biomass through pyrolysis, has a potential soil amendment and carbon sequestration medium [3]. Pyrolysis is a thermo chemical process where biomass is heated in the absence of oxygen, whereby the resulting char is primarily stabilized carbon [4]. Pyrolysis can be optimized to produce a number of primary and secondary products such as synthesis gas with differing energy values (syngas), liquid and char [5]. When char is intentionally produced for agricultural or environmental use it is called biochar. When used as a soil amendment, biochar applied to the soil has been reported to boost soil fertility and improve soil quality resulting in increased crop yields. Soil benefits include raising soil pH, increasing moisture holding capacity, attracting more beneficial fungi and microbes, improving cation exchange capacity (CEC) and retaining nutrients [6, 7]. These benefits have been shown to increase yield in biomass and crops under variable conditions [8, 9, 10].

The term “biochar” is relatively new, yet biochars in one form or another have been used throughout history, mainly for soil improvement. One of the first historical mentions of biochar use for soil improvement dates back at least 2000 years [11]. In the Amazon Basin, there exists evidence of extensive use of biochar in the fertile soils known as Terra Preta (black soil) and Terra Mulata (mulatto earth), which were created by ancient, indigenous cultures of the time most likely to enhance localized soil productivity. To this day, the terra preta soils in the region remain highly fertile compared with other soils of the region like Oxisols and Ultisols, often containing as much as 4 times more organic matter in the top 30 cm of the soil [12]. Thus, the objective of this paper is to review the potential agronomic benefits and carbon sequestration ability of biochar.

Production of Biochar from Different Biomasses:

Biochar is made from variety of biomasses that have different physicochemical properties. The properties of each biomass feedstock are important in thermal conversion processes, particularly the proximate analysis such as, ash and moisture content, fractions of fixed carbon and volatile components percentage and composition of inorganic substance, bulk density, particle size and moisture content [13]. Extensive feedstock biomasses have been used in the production of biochar, such as bioenergy crops: willows, miscanthus and switchgrass [14,15], forest residues: sawdust, grain crops and nut shells) [16], organic waste: green yard waste and animal manure [17], agricultural waste [18], kitchen waste and sewage sludge [19]. In general, a high yield of biochar derived from this biomass which has more lignin and less cellulose can be expected. Biochar can be produced both

in traditional earthen charcoal kilns, where pyrolysis, gasification and combustion process are carried out in parallel below the earthen kiln layer and in modern biochar, where pyrolysis and combustion processes are physically separated by a metal barrier [20].

Pyrolysis technology can be distinguished by the residence time, pyrolytic temperature of the pyrolysis material (slow and fast pyrolysis process), pressure, size of adsorbent and the heating rate and method (pyrolysis started by the burning of fuels, by electrical heating, or by microwaves). Asensio *et al.* [20], differentiate pyrolysis technology according to the pyrolytic temperature and the residence time of the pyrolysis or carbonization process. Slow pyrolysis (heating for seconds or minutes) may be described as a continuous process, where purged (oxygen-free) feedstock biomass is transferred into an external heated kiln or furnace (gas flow removing volatile biochar emerging at the other end); “fast” pyrolysis on the other hand depends on very quick heat transfer, typically to fine biomass particles at less than 650 °C with rapid heating rate [21]. The characteristics of the biochar product are heavily affected by the extent of pyrolysis (pyrolytic temperature and residence pressure) and entirely by biomass size and kiln or furnace residence time. The rate at which volatile and gases are removed in a kiln or furnace determines the vapour residence time. Prolonged residence time results in secondary reactions, notably the reactions of tar on biochar surfaces and charring of the tar rather than additional combustion or processing outside the kiln or furnace [22]. For gasification in pyrolysis, the biomass feedstock to some extent is oxidized in the gasification chamber at a temperature of about 800 °C at atmospheric or elevated pressure [23].

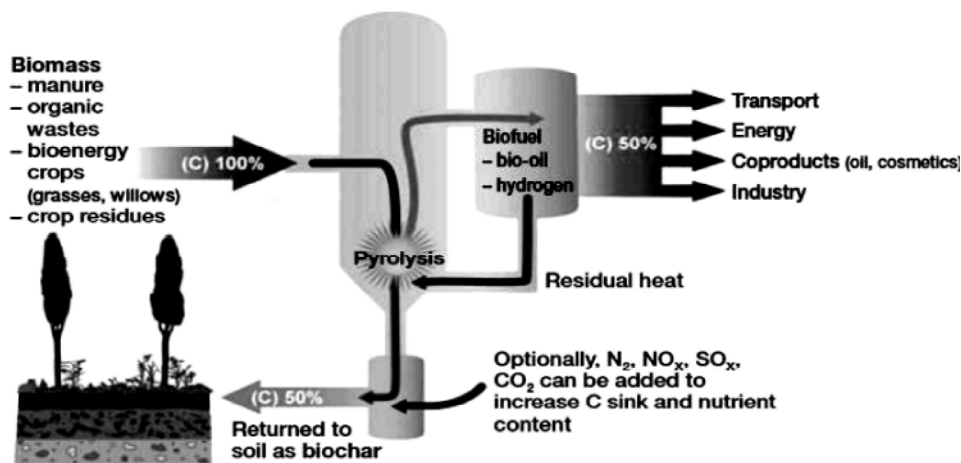


Fig. 1: Schematic of pyrolysis process for the production of biochar. Adopted from Lehmann (2007)

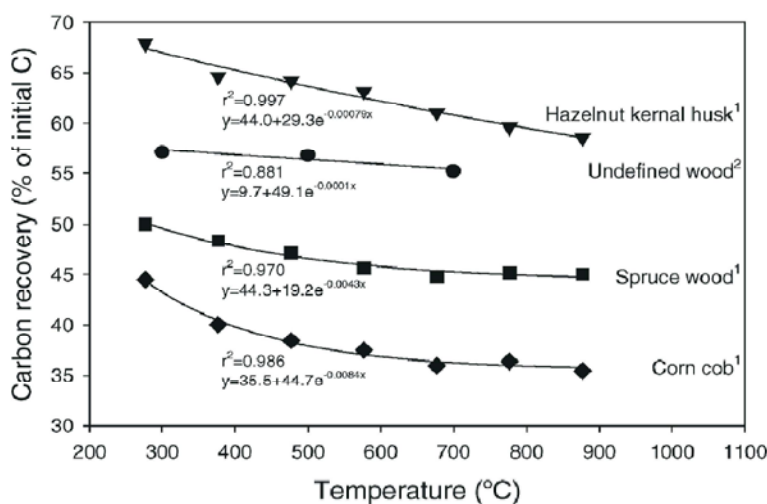


Fig. 2: Carbon recovery in biochar with increasing temperature using pyrolysis of different types of biomass from [24]

The pyrolysis temperature typically changes the yield of biochar as well as the properties of biochar. With increasing temperature, the recovery of biochar commonly decreases whereas the C concentration increases [25, 26]. This leads to only a slightly lower C recovery in biochar as pyrolysis temperatures increase (Fig. 2). The temperature dependency above 350°C is low, since the weight loss is compensated by an almost equivalent increase in C concentration. Therefore, pyrolysis temperature does not significantly affect C sequestration balances. More important than temperature for C yields in biochar is the type of biomass used for pyrolysis. Other factors that decrease biochar yields are higher sweep gas flow, smaller particle sizes [27] and higher heating rates [28].

Properties of Biochar

Physiochemical Properties of Biochar: The biochar produced at different pyrolytic temperature had a distinguishable honey-comb-like structure. As a result of these well-developed pores, the biochar possessed a high surface area. The form, type, preliminary preparation steps and size of the biomass feedstock and type of pyrolysis product may affect the characteristics, nature, quality and potential use of biochar. Initially, the ratio of exposed to total surface area of biochar will be affected by its size. Additionally, although low pyrolytic temperature biochar is stronger than high temperature products, it is brittle and pores are grinded into fine fractions once incorporated into the soil [29].

The chemical characteristics of individual feedstock species and therefore biochar derived from the feedstock have always been shown to vary significantly both spatially and temporarily [30]. Biochar production is often

assessed through changes that might occur in the elemental concentrations of C, H, O, S and N and associated ratios [31]. It is well known that fixed carbon is the solid combustible residue that remains after a particle sample is carbonized and volatile matter is expelled [32, 33]. Thus, it is used as an estimate of the number of carbonaceous substances that will be yielded from a solid sample. Particularly, H/C and O/C ratios are used to determine the degree of aromaticity and maturation [34]. Elemental ratios of O/C, O/H and C/H have been found to provide a reliable measure of both the extent of pyrolysis and level of oxidative adjustment of biochar in the soil and solution systems and are relatively straightforward to be determined [35].

Biochar contains some ash content, which adds some nutrients and typically has an alkaline pH and high cation exchange capacity (CEC) [36]. Though different biochars share these basic characteristics. All biochars have different specific characteristics depending on the properties of the starting organic material (feedstock) and the pyrolysis parameters used for production [37]. For instance a wood derived biochar will contain a higher proportion of carbon than a manure biochar due to starting differences in carbon content. In turn a manure biochar will contain more ash than wood biochar due to higher nutrient content in manure [38, 39]. The pyrolysis heating temperature and duration can vary and has an important impact on a biochar’s final chemical properties. As production temperature increases the pH and CEC increases, carbon content becomes concentrated, proportion of labile carbon content decreases and proportion of recalcitrant carbon content increases [40, 41]. Labile carbon refers to forms of carbon that are more readily broken down in the soil and recalcitrant refers to

Table 1: Some physicochemical properties of selected biochars [44]

Feedstock	Temperature (°C)	pH	CEC (cmol/kg)	C (%)	C/N	Total P (mg/kg)	Ash (%)	Volatiles (%)	Fixed (C %)	H/C	O/C	SSA (m ² /g)
Oak wood	60	3.73	182.1	47.1	444	5	0.3	88.6	11.1	1.48	0.72	-
	350	4.80	294.2	74.9	455	12	1.1	60.8	38.1	0.55	0.20	450
	600	6.38	75.7	87.5	489	29	1.3	27.5	71.2	0.33	0.07	642
Corn stover	60	6.70	269.4	42.6	83	526	8.8	85.2	6.0	1.56	0.74	-
	350	9.39	419.3	60.4	51	1889	11.4	48.8	39.8	0.75	0.29	293
	600	9.42	252.1	70.6	66	2114	16.7	23.5	59.8	0.39	0.10	527
Poultry litter	60	7.53	363.0	24.6	13	16,685	36.4	60.5	3.1	1.51	1.03	-
	350	9.65	121.3	29.3	15	21,256	51.2	47.2	1.6	0.57	0.41	47
	600	10.33	58.7	23.6	25	23,596	55.8	44.1	0.1	0.18	0.62	94

forms of carbon resistant to decay. As a result of feedstock and pyrolysis variability, there is a wide variation in physical and chemical properties of biochars, which in turn contributes to the variability of its impact when used as an agricultural soil amendment [38].

Nutrient Values of Biochar: Some biochars are a potential source of nutrients (Table 1). The nutrient content of biochar is largely determined by biomass feedstocks [42]. Feedstocks with higher nutrient contents such as animal manures will produce biochars with greater nutrient value, compared with plant feedstocks [43].

Pyrolysis temperature also affects nutrient value: for example, analysis of two biochars produced under different temperatures (450 and 600°C) from the same poultry litter feedstock revealed a lower total phosphorus (21,256 mg/kg) and higher total P(23,596 mg/kg) for the lower temperature product compared with the higher temperature product, respectively. Furthermore, the concentration of C and N may increase with increasing pyrolysis temperature in plant-based biochars, but the C and N concentrations may decrease with increasing pyrolysis temperature for mineral-rich feedstocks, such as manure, because less-volatile elements, including P, K, Ca and Mg, are concentrated as the volatiles are lost. However, information on forms and bioavailability of nutrients present in biochars is scarce and some research has shown that feedstock type and pyrolysis temperature can significantly influence bioavailable fraction of nutrients in biochars [42].

Stability of biochar: The stability of organic matter in soils is determined by its ability to resist microbial and chemical decomposition, through chemical transformations and physical interactions with soil minerals. Biochar, has a predominantly condensed aromatic structure that is known to be highly resistant to microbial decomposition [45]. Additionally, interactions of biochar with soil minerals could further increase stability of biochar in soil [46], further contributing to long-term carbon sequestration [3], while also adding to the health and production outcomes of soil systems. Different published studies have reported soil residence time of

biochars in time scales ranging from decades to centuries to millennia [14,47]. The stability of biochar depends on the type of biomass feedstock, charring conditions (temperature, heating time), biochar particle size and climatic conditions under which biochar oxidises [3, 44]. In general, the proportion of aryl-C to aliphatic-C in biochar increases with increasing charring or pyrolysis temperature [48]. The liability and density of the biomass feedstock and its mineral content may also influence the decomposition rate of biochar in soil [49].

Spectroscopic and surface chemistry analyses have proven useful to evaluate biochar–mineral interactions and oxidation status of biochar along a decomposition continuum [50]. However, these approaches do not quantify turnover time, necessary to evaluate the residence time of biochar in soil. The rate of biochar decomposition may vary according to the stability of the oxidisable component, i.e. initial rapid decomposition of surface oriented labile components of the biochar particle (e.g. aliphatic-C) followed by slow decomposition of condensed aromatic-C, which dominates the core structure of biochar. This warrants long-term studies to accurately estimate the mean residence time of biochar in soil [44]. Furthermore, biochars can potentially stimulate decomposition of native soil organic matter (i.e. humic and labile components) possibly by enhancing microbial activity [51]. However, application of biochar may also lead to a decline in the decomposition of other organic matter components, through the possible enhancement of soil aggregation [52]. The “priming effect” of biochar on organic matter decomposition in soil needs to be accounted for to determine the magnitude of biochar decomposed. Carbon isotope methods (¹³C, or ¹⁴C/¹³C labeling) can be used to identify sources of C decomposed in biochar–soil systems [53]. These methods can be relatively easy to manage in the laboratory, providing optimal conditions for biochar decomposition. However, in the field, presence of plant roots, rhizosphere processes and variable environmental conditions provide challenges to identifying C sources with a limited number of isotopes [47].

Effects of Biochar on Soil Properties

Effects of Biochar on Soil Physicochemical Properties:

Soils have different physicochemical and biological characteristics, depending on the nature of the mineral matrix, the organic matter and the way they are associated [54]. However, when materials with different characteristics are present, there may be changes in the properties of the soil, changing the characteristics. Due to its higher specific surface area, the presence of biochar may contribute to significant changes in the soil physical properties by changing its texture, structure, consistency and porosity, pore size, size distribution and density. According to Downie *et al.* [36], the change in the soil physical properties due to the presence of biochar may result in increased plant growth because there is an increase in water availability in the area close to the root system that is mainly determined by the physical composition of soil horizons. Because of its porosity and, consequently, its high specific surface area, biochar can significantly increase the capacity of water retention, especially in sandy soils [55].

All of these changes in the physical soil properties can lead to changes in the chemical and biological properties of the soil due to the availability of chemically reactive groups and habitats for soil microorganisms [54]. The specific surface area of soil is an extremely important feature that influences fertility, water and air availability, nutrient cycling and microbial activity [56]. The specific surface area of biochar, approximately 200 to 400 m² g⁻¹, is comparable to that of the clay fraction. The cation exchange capacity (CEC) is associated with the specific surface area, but it is highly dependent on chemically reactive sites, which are formed over years during microbial degradation, altering the chemical and physical characteristics of biochar. According to Cohen-Ofri *et al.* [55], these changes result from the increase of electric charges arising from the oxidation of biochemical compounds, leading to an increase in phenolic, hydroxyl, carbonyl and quinone compounds and, consequently, an increase in the overall negative surface charge that results from the replacement of positive charges in the oxidation process.

Cation exchange capacity (CEC) is a measure of the ability of a substrate to retain positively charged ions through electrostatic forces. Biochar has been associated with the enhancement in CEC of some amended soils, thereby increasing the availability and retention of plant nutrients in soil and potentially increasing nutrient use efficiency. However, biochars from different feedstocks and produced under differing pyrolysis conditions may

differ in surface charge properties. Of the two biochars from the same peanut hull biomass, the biochar produced at 500°C had a lower CEC (4.63 cmol/kg) compared with that produced at 400°C (14.2 cmol/kg). The reduction in surface functional groups was suggested as the cause of lower CEC in the biochar produced at higher temperatures. The decline in the acidic functional groups on biochar surfaces has been reported to be greatest between 300 and 400°C [57]. Liang *et al.* [58], reported that the high charge density (CEC/specific surface area) of “aged” biochar resulted from oxidation of the particles and adsorption of organic matter to biochar surfaces. An increase in the charge density on biochar surfaces as biochar interacts with soil over time [59] could be responsible for enhanced cation retention and consequently reduced leaching from amended soils [49]. However, more research on the chemical interactions of differing biochars and soils, as well as the implications for soil nutrient retention, is needed.

Effects of Biochar on Biological Properties Soil:

The porous structure of biochar, its high internal surface area and its ability to adsorb soluble organic matter, gases and inorganic nutrients are likely to provide a highly suitable habitat for microbes to colonize, grow and reproduce, particularly for bacteria, actinomycetes and arbuscular mycorrhizal fungi. Some members of these groups may preferentially colonize biochar surfaces depending upon the physical and chemical characteristics of different biochars [60].

The pore space of pyrolysed biomass increases during charring by several thousand folds and is related to charring temperature and feedstock materials. Estimates of the resulting surface area of different biochars range from 10 to several hundred square meters per gram (m² g⁻¹), which provides a significantly increased surface area for microbial colonization. Several authors have suggested that the biochar pores may act as a refuge site or microhabitat for colonizing microbes, where they are protected from being grazed upon by their natural predators or where microbes that are less competitive in the soil environment can become established. The pore size variation observed across biochar particles from different feedstocks and pyrolysis conditions is such that the microflora could, indeed, colonize and be protected from grazing, especially in the smaller pores [61].

The high porosity of biochar may also allow it to retain more moisture. An increase in the water holding capacity (WHC) of biochar may result in an overall increase in the WHC of the soils to which it is added.

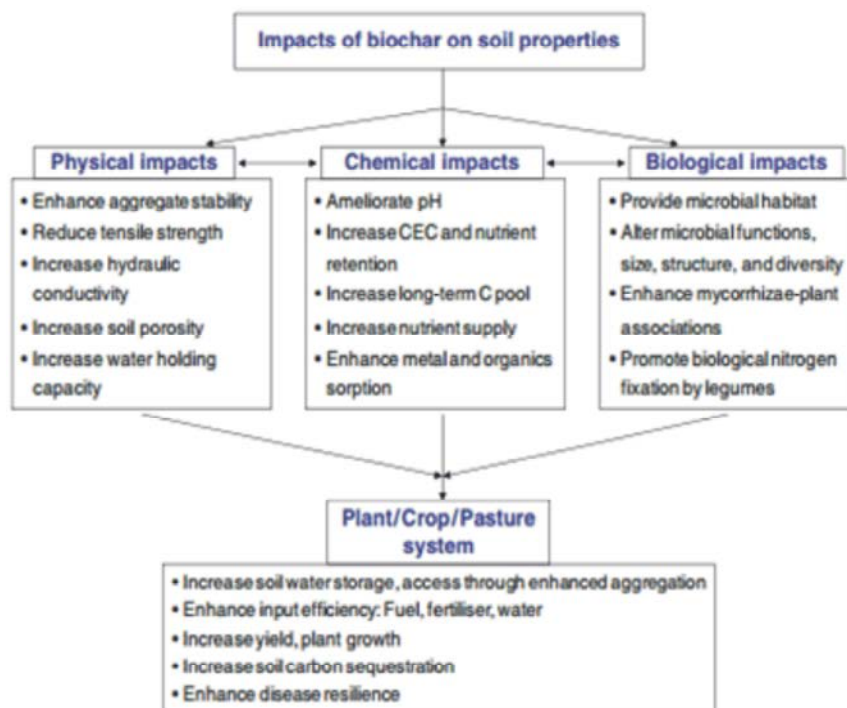


Fig. 3: Potential impacts of biochar application to plant–soil systems. Adopted from [64]

For biochars with a high mineral-ash content, the porosity will continue to increase as the ash is leached out over time; thus, the capacity of the biochar to retain water, provide surfaces for microbes to colonize and for various elements and compounds to become adsorbed is also likely to increase over time. Smaller pores will attract and retain capillary soil water much longer than larger pores (larger than 10µm to 20µm) in both the biochar and the soil. Water is the universal biological solvent and its presence in biochar pores increases the ‘habitability’ of biochar substantially [62].

In addition to water, a variety of gases, including carbon dioxide (CO₂) and oxygen (O₂), will be dissolved in pore water, occupy the air-filled pore space or be chemisorbed onto biochar surfaces; this latter is due to the defect structures present in the amorphous and micro-graphene lattices. Depending upon the ratio of air- to water filled pore space, the relative concentrations of the gases, their diffusion rates and the extent of surface sorption, either aerobic or anaerobic conditions will predominate in the biochar pores. Where sufficient O₂ is available, aerobic respiration will be the dominant metabolic pathway for energy generation, resulting in water (H₂O) and CO₂ as the primary metabolic end products. As the O₂ concentration decreases, facultative aerobes will begin to use anaerobic respiratory pathways

as long as suitable terminal electron acceptors are available. Thus, O₂ diffusion into biochar pores and the terminal electron acceptor used during microbial respiration will, in large part, determine what the remaining pore atmosphere will contain and how hospitable this environment is likely to be for its occupants [63].

Biochars vary considerably in their pH, depending upon feedstock and pyrolysis temperature and, thus, will also vary in the microbial communities that develop on and around them. Under the extremes of pH, fungi will probably predominate due to their wide range of pH tolerance; most bacteria prefer circum-neutral pH. Adding biochar to soil, whether acid or alkaline, may lead to significant changes in the soil community composition by changing the overall ratio of bacteria to fungi, as well as the predominance of different genera within these populations [3].

Biochar Application Rate to Soil and Crop Responses:

Along with improved soil health, increased crop yield is generally reported with application of biochar to soils. However, many of the published experiments are highly variable and dependent on many factors, mainly the initial soil properties and conditions and biochar characteristics. Positive crop and biomass yield was found for biochar produced from wood, paper pulp, wood chips and poultry

litter [65]. In some studies corn yield was improved 140% (Major et al., 2010), cowpea by 100%, while radishes grown with poultry litter biochar yielded a 96% increase [66].

A meta-analysis of the available literature performed by Jeffery *et al.* [65], found a 10% mean yield increase in crop productivity as a percentage of the control at application rates of 10, 25, 50 and 100 t/ha. These findings were confirmed by Biederman and Harpole [67]. Liu *et al.* [68] reviewed published data from 59 pot experiments and 57 field experiments from 21 countries and found crop productivity was increased by 11% on average. They found benefits at field application rates typically below 30 t/ha field application and reported that increases in crop productivity varied with crop type with greater increases for legume crops (30%), vegetables (29%), corn (8%), wheat (11%) and rice (7%).

Biederman and Harpole [67], analyzed the results of 371 independent studies. This meta-analysis showed that the addition of biochar to soils resulted in increased aboveground productivity, crop yield, soil microbial biomass, rhizobia nodulation, plant K tissue concentration, soil phosphorus (P), soil potassium (K), total soil nitrogen (N) and total soil carbon (C) compared with control conditions. They found that variability in crop production increased with application rates.

Hossain *et al.* [69], applied wastewater sludge biochar at 10 t/ha to cherry tomatoes resulting in increased production by 64% above the control soil conditions. The yield gains were attributed to the combined effect of increased nutrient availability (P and N) and improved soil chemical conditions resulting from the biosolid based amendment. However, there appears to be an upper limit on the application of biochar additions and crop productivity. Lehmann *et al.* [6], notes that crops respond positively to biochar additions up to 55 t/ha, showing growth reductions only at very high applications.

The findings of Biederman and Harpole [67] also confirmed instances of decreasing yield due to a high biochar application rate. When the equivalent of 165 t/ha of biochar was added to a poor soil in a pot experiment, yields decreased to the level of the unamended control. Others have reported thresholds at much lower levels. Asai *et al.* [70], reported greater rice yields with 4 t/ha of biochar compared with 8 or 16 t/ha applied, with the higher application rates providing yields not different from the unamended control. The reasons for these decreases are not known; further study is necessary to determine which biochar materials are best suited for

application and at which rates to specific soils. Therefore, the recommended application rates of biochar as a soil amendment are quite variable given the insufficient field data available to make general recommendations on biochar application rates according to soil types and crops.

Carbon Sequestration Potential of Biochar: Climate change is one of the most critical important issues that challenge facing the modern world. Temperature increases have now been unequivocally proven and are occurring with an unprecedented rate [71]). Carbon dioxide (CO₂), methane (CH₄) and nitrous oxides (NO_x) are important drivers of the anthropogenic greenhouse effect, which are released both through burning of fossil and biomass fuel as well as decomposition of above- and belowground organic matter. International efforts aim at reducing avoidable greenhouse gas emissions or off-setting unavoidable emissions through sequestration of C in the environment. As regards sequestration, many different strategies were discussed, ranging from wide-spread afforestation and reforestation in terrestrial ecosystems to pumping of CO₂ into deep ocean and geological layers [72]. For terrestrial ecosystems it has been proposed that C sequestration can be increased by increasing soil C stocks [73, 74]. Such a proposal is sensible given the fact that more than 80% of the terrestrial organic C stores are contained in soils [72]. However, recent analyses urge caution, highlighting that efforts aimed to achieve C sequestration in soil are often off-set by other greenhouse gas emissions and that soils generally show low potential to accumulate C. For example, in conjunction with forest growth [75]. The consensus appears to be that soil represents a finite C sink at best and will only provide a window of opportunity for reducing C emissions or exploring other opportunities for C sequestration and that these C sinks may have a low permanency and can be easily depleted upon land use change [76,77].

A new approach to C sequestration in terrestrial ecosystems through the application of biomass-derived black C called “biochar” to soil, which offers both a large and long-term C sink. The conversion of biomass to biochar as a C sink has been proposed before [78] but was not plainly linked to an application to soil. Application of biochar to soil is not a new concept. For example, certain dark earths in the Amazon Basin (so-called Amazonian Dark Earths or “*terra preta*”) have received large amounts of charred materials, the residues from biomass burning [79]. These applications were most likely a result of both

habitation activities and deliberate soil application by Amerindian populations before the arrival of Europeans [80]. Large amounts of biochar derived C stocks remain in these soils today, hundreds and thousands of years after they were abandoned. The total C storage is as high as $250\text{MgCha}^{-1}\text{ m}^{-1}$ compared to typical values of $100\text{MgCha}^{-1}\text{ m}^{-1}$ in Amazonian soils derived from similar parent material. Such C storage in soils far exceeds the potential C sequestration in plant biomass even if bare soil were, theoretically, restocked to primary forest containing about 110MgCha^{-1} above ground [79].

Mechanism and Quantification of Carbon Sequestration in Biochar:

Conversion of biomass to biochar fundamentally alters the transformation dynamics with respect to C sequestration. Upon charring approximately 50% of the C contained in the biomass is immediately released, leaving a stable biochar residue (Fig. 4A). Non biochar material decomposing in soil will initially release C more slowly over time. However, release of C continues until almost all C is lost and can be estimated to be less than 10–20% C remaining in agricultural soil after 5–10 years (depending on C quality and environment). Thus ultimately the biochar application leads to considerably greater amounts of C remaining in soil than application of uncharred organic matter.

Under normal circumstances CO_2 is removed from the atmosphere by photosynthesis and added to the soil in the form of organic matter, then as the organic matter decomposes CO_2 is released back into the atmosphere though microbial respiration. The pyrolysis of organic matter results in a form of carbon with an altered chemical structure (aromatic C rings) that is resistant to microbial decomposition, called recalcitrant or fixed carbon. When added to the soil this carbon is not readily decomposed and hence carbon remains in the soil and out of the atmosphere [6].

Carbon dating studies measuring the age of biochar derived carbon in the environment [80, 81] and laboratory incubation studies measuring decomposition rates over short periods of time [50, 44], have both demonstrated a potential lifespan in the range of hundreds to thousands of years for biochar derived carbon in the soil. To highlight the difference between biochar and compost, it has been estimated that biochar can on average sequester 25-50% of its feedstock's carbon for 100s to 1000s of years, whereas compost or organic residue additions sequester 10-20% of its feedstock's carbon for 5 -10 years [6].

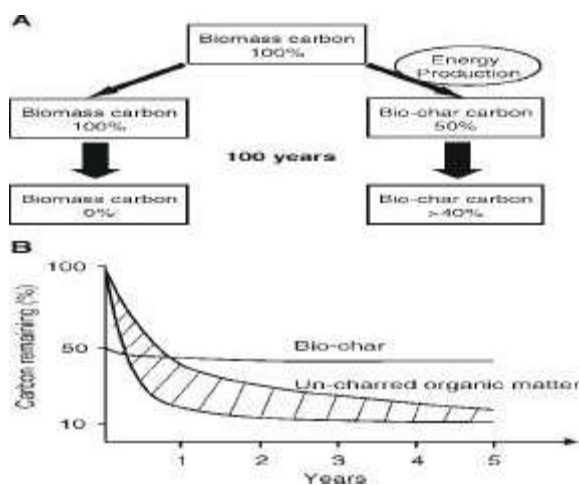


Fig. 4: A) C remaining from biomass decomposition after 100 years; C remaining after charring or pyrolysis ; bio-char C remaining after decomposition. (B) Range of biomass C remaining after decomposition of crop residues; estimation of bio-char decomposition [82].

The global potential for annual sequestration of atmospheric CO_2 through biochar application has been estimated at the billion-tonne scale (Gt/year) under present day scenarios. The greenhouse gas mitigation potential from the application of biochar to agricultural systems may vary widely with variation in biomass feedstock, production technologies, product utilization methods and environmental conditions [83].

CONCLUSIONS

The agronomic benefits of biochar as a soil improvement for sustainable agriculture and its ability to carbon sequestration was reviewed in this paper to some extent. The high nutrient contents and nutrient retention capacity of biochar lead to improved nutrient supply for plants and reduced nutrient losses by leaching. Nutrients are physically trapped in the fine pores of amorphous carbonized materials and slow biological oxidation produces carboxylic units on the edges of the condensed aromatic backbone of the biochar which increases the CEC. Transformation of labile plant organic matter into stable C pools can reduce the release of the greenhouse gas CO_2 into the atmosphere during land clearing and can increase C sequestration in the soil. There are strong indications that biochar is very slowly mineralized in the soil environment. Using biochar as an instrument for

improving soil fertility, while at the same time increasing C sequestration in soil is far from being a well-recognized technology. However, the demonstrated positive effects of biochar additions on soil properties and productivity should stimulate further investigations. Future research needs to focus on testing biochar amendments in experimental plots and under field conditions and achieving a better understanding of physicochemical properties of biochar surfaces. Finally, an evaluation of the agronomic effectiveness and the economic viability of biochar as a soil amendment under field conditions are needed. The decomposition rate of biochar in soil is still poorly understood. However, quantitative prediction of sorption capacity remains to be a challenge for biochars. As the impacts of biochar on soil processes may change over time, there is a need for long-term studies to assess biochar's potential to provide its benefits. Measures to secure sustainable feedstock supply and novel biochar processing technologies are needed to ensure that biochar production delivers net environmental benefits. Measures could include certification against an agreed standard, similar to the sustainability certification undertaken in the forestry sector and being developed for bioenergy. Government incentives for commercial demonstration are needed to enable the technologies to become an acceptably low-risk proposition in a free market economy. With the possibility of multiple environmental benefits from its use, biochar-amended systems may become a vital tool to mitigate climate change and enhance the sustainability and productive capacity of global environmental systems.

REFERENCES

1. Bot, A. and J. Benites, 2005. The Importance of Soil Organic Matter: Key to Drought-Resistant Soil and Sustained Food Production; FAO UN: Rome, Italy.
2. Erisman, J.W., M.A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, 2008. How a century of ammonia synthesis changed the world. *Nat. Geosci.*, 1: 636-639.
3. Lehmann, J. And S. Joseph., 2009. Biochar for environmental management: An introduction. In: Lehmann J, Soseph S, (ed). *Biochar for environmental management: Science and Technology*. 1st Ed. Londres: Earthscan 4-18.
4. Yaman, S., 2004. 'Pyrolysis of biomass to produce fuels and chemical feedstocks', *Energy Conversion and Management* 45: 651-671.
5. Bridgwater, A.V., 2003. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* 91:87-102.
6. Lehmann, J., J. Gaunt and M. Rondon, 2006. Bio-char sequestration in terrestrial ecosystems - A review. *Mitigation and Adaptation Strategies for Global Change*, 11: 403-427.
7. Lehmann, J., 2007. Bio-energy in the black. *Front. Ecol. Environ.*, 5: 381-387.
8. Steiner, C., W. Teixeira, J. Lehmann, T. Nehls, de J. Mace^do, W. Blum and W. Zech, 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant Soil*, 291: 275-290.
9. Rondon, M.A., J. Lehmann, J. Ramirez and M. Hurtudo, 2007. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions, *Biology and Fertility of Soils*, 43(6): 699-708.
10. Chan, K.Y., L. Van Zwieten, I. Meszaros, A. Downie, S. Joseph, 2007. Agronomic values of greenwaste biochar as a soil amendment. *Aust J Soil Res.*, 45: 629-634.
11. O'Neill, B., J. Grossman, M.T. Tsai, J.E. Gomes, J. Lehmann, J. Peterson, E. Neves and J.E. Thies, 2009. Bacterial community composition in Brazilian Anthrosols and adjacent soils characterized using culturing and molecular identification. *Microb. Ecol.*, 58: 23-35.
12. Glaser, B., L. Haumaier, G. Guggenberger and W. Zech, 2001. The "Terra Preta" phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften*, 88: 37-41.
13. Angin, D., 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology*, 128: 593-597.
14. Zimmerman, R.A., N.G. Kasozi, P. Nkedi-Kizza and B. Gao, 2010. Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars), *Environmental Science and Technology*, 44: 6189-6195.
15. Beeseley, L. and M. Marmiroli, 2011. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar, *Environmental Pollution*, 159(2): 474-480.

16. Xu, T., L. Lou, R. Cao, D. Duan and Y. Chen, 2012. Effect of bamboo biochar on pentachlorophenol leachability and bioavailability in agricultural soil, *Science of the Total Environment*, 414: 727-731.
17. Song, W. and M. Guo, 2012. Quality variations of poultry litter biochar generated at different pyrolysis temperatures, *Journal of Analytical and Applied Pyrolysis*, 94: 138-145.
18. Zhao, X., W. Ouyang and F. Hao, 2013. Properties comparison of biochars from corn straw with different pretreatment and sorption behaviour of atrazine, *Bioresource Technology*, 147: 338-344.
19. Lu, H., W. Zhang, Y. Yang, X. Huang, S. Wang, R. Qiu, 2012. Relative distribution of Pb²⁺ sorption mechanisms by sludge-derived biochar, *Water Research*, 46(3): 854-862.
20. Asensio, V., F.A. Vega, M.L. Andrade and E.F. Covelo, 2013. Tree vegetation and waste amendments to improve the physical condition of copper mine soils, *Chemosphere*, 90(2): 603-610.
21. Meyer, S., B. Glaser and P. Quicker, 2011. Technical, economical and climate-related aspects of biochar production technologies: a literature review, *Environmental Science and Technology*, 45(22): 9473-9483.
22. Oliver, D.P., Y.F. Pan and J.S. Anderson, 2013. Sorption of pesticides by a mineral sand mining by-product, neutralized used acid (NUA), *Science of the Total Environment*, 442: 255-262.
23. Bridgwater, A.V., 2007. The production of biofuels and renewable chemicals by fast pyrolysis of biomass, *International Journal of Global Energy Issues*, 27(2): 160-203.
24. Demirbas, A., 2001. Carbonization ranking of selected biomass for charcoal, liquid and gaseous products, *Energy Conversion and Management*, 42: 1229-1238.
25. Daud, W.M.A.W., W.S.W. Ali and M.Z. Sulaiman, 2001. Effect of carbonization temperature on the yield and porosity of char produced from palm shell, *Journal of Chemical Technology and Biotechnology*, 76: 1281-1285.
26. Katyal, S., K. Thambimuthu and M. Valix, 2003. Carbonisation of bagasse in a fixed bed reactor: influence of process variables on char yield and characteristics, *Renewable Energy*, 28: 713-725.
27. Zanzi, R., K. Sjöström and E. Björnborn, 2002. 'Rapid pyrolysis of agricultural residues at high temperature, *Biomass and Bioenergy*, 23: 357-366.
28. Demirbas, A., 2004b. Determination of calorific values of bio-chars and pyro-oils from pyrolysis of beech trunkbarks, *Journal of Analytical and Applied Pyrolysis*, 72: 215-219.
29. Harmsen, J. and R. Naidu, 2013. Bioavailability as a tool in site management, *Journal of Hazardous Materials*, 261: 840-846.
30. Zhang, W.F., Z.X. Dou, X.T. He P. Ju, D. Powlson, D. Chadwick, D. Norse, Y.L. Lu, Y. Zhang and L. Wu, 2013. New technologies reduce greenhouse gas emissions from nitrogenous fertilizer in China. *Proc. Natl. Acad. Sci. USA* 110: 8375-8380.
31. Smernik, R.J., J.A. Baldock, J.M. Oades and A.K. Whittaker, 2002. Determination of T1ρH relaxation rates in charred and uncharred wood and consequences for NMR quantitation, *Solid State Nuclear Magnetic Resonance*, 22(1): 50-70.
32. Murage, E.W., P. Voroney and R.P. Beyaert, 2007. Turnover of carbon in the free light fraction with and without charcoal as determined using the 13C natural abundance method. *Geoderma*, 138: 133-143.
33. Haeefele, S.M., Y. Konboon and W. Wongboon, 2011. Effects and fate of biochar from rice residues in rice-based systems, *Field Crops Research*, 121(3): 430-440.
34. Hammes, K., R.J. Smernik, J.O. Skjemstad and M.W.I. Schmidt, 2008. Characterization and evaluation of reference materials for black carbon analysis using elemental composition, colour, BET surface area and C-13 NMR spectroscopy. *Appl Geochem.*, 23: 2113-2122.
35. Yu, J.T., A.M.N. Dehkoda and Ellis, 2011. Development of biochar-based catalyst for transesterification of canola oil, *Energy and Fuels*, 25(1): 337-344.
36. Dowie, A., A. Crosky and P. Muroe, 2009. Physical properties of biochar, in *BC for Environmental Management*, Lehmann J. and Joseph S, Eds., Earthscan, London, UK 47-82,.
37. Chan, K.Y. and Z.H. Xu, 2009. Biochar - Nutrient properties and their enhancement. In: *Biochar for Environmental Management: Science and Technology* (eds. Lehmann J. and Joseph S). Earthscan Ltd. London.
38. Novak, J.M., W.J. Busscher, D.L. Laird, M. Ahmedna, D.W. Watts and M.A.S. Niandou, 2009. Impact of biochar amendment on fertility of a Southeastern coastal plain soil. *Soil Sci.*, 174: 105-112.

39. Singh, B.P., B.J. Hatton, B. Singh, A.L. Cowie and A. Kathuria, 2010. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *Journal of Environmental Quality*, 39: 1224-1235.
40. Keiluweit, M., P.S. Nico, M.G. Johnson and M. Kleber, 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental Science & Technology*, 44: 1247-1253.
41. Peng, X., L.L. Ye, C.H. Wang, X. Zhou and B. Sun, 2011. Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil & Tillage Research*, 112: 159-166.
42. Gaskin, J.W., C. Steiner, K. Harris, K.C. Das and B. Bibens, 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans ASABE* 51: 2061-2069.
43. Singh, B., B.P. Singh and A.L. Cowie, 2010b. Characterization and evaluation of biochars for their application as a soil amendment. *Aust J Soil Res.*, 48: 516-525.
44. Nguyen, B.T. and J. Lehmann, 2009. Black carbon decomposition under varying water regimes. *Org Geochem.*, 40: 846-853.
45. Baldock, J.A. and R.J. Smernik, 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Org Geochem*, 33: 1093-1109.
46. Brodowski, S., B. John, H. Flessa and W. Amelung, 2006. Aggregate-occluded black carbon in soil. *Eur J Soil Sci.*, 57: 539-546.
47. Major, J., M. Rondon, D. Molina, S.J. Riha and J. Lehmann, 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant Soil*, 333: 117-128.
48. Nguyen, B.T., J. Lehmann, W.C. Hockaday, S. Joseph and C.A. Masiello, 2010. Temperature sensitivity of black carbon decomposition and oxidation. *Environ Sci Technol.*, 44: 3324-3331.
49. Singh, B.P., B.J. Hatton, B. Singh, A. Cowie and A. Kathuria, 2010a. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J Environ Qual.*, 39: 1224-1235.
50. Liang, B., J. Lehmann, D. Solomon, S. Sohi, J.E. Thies, J.O. Skjemstad, F.J. Luizao, M.H. Engelhard, E.G. Neves and S. Wirrick, 2008. Stability of biomass-derived black carbon in soils. *Geochim Cosmochim Acta.*, 72:6069-6078.
51. Wardle, D.A., M.C. Nilsson and O. Zackrisson, 2008. Fire-derived charcoal causes loss of forest humus. *Science*, 320: 629
52. Liang, B.Q., J. Lehmann, S.P. Sohi, J.E. Thies, B. O'Neill, L. Trujillo, J. Gaunt, D. Solomon, J. Grossman, E.G. Neves and F.J. Luizao, 2010. Black carbon affects the cycling of non-black carbon in soil. *Org Geochem.*, 41: 206-213.
53. Kuzyakov, Y., I. Subbotina, H.Q. Chen, I. Bogomolova and X.L. Xu, 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by C-14 labeling. *Soil Biol Biochem.*, 41: 210-219.
54. Brady, N.C. and R.R. Weil, 2008. *The nature and properties of soils*. 14th Ed., Upper Saddle River: Prentice Hall, 965.
55. Cohen-Ofri, I., R.L. Weine, E. Boaretto, G. Mintz and S. Weiner, 2006. Modern and fossil charcoal: aspects of structure and diagenesis. *Journal of Archaeological Science*, 33: 428-439.
56. Kolb, S.E., K.J. Fermanich and M.E. Dornbush, 2009. Effect of charcoal quantity on microbial biomass and activity in temperate soils. *Soil Biology & Biochemistry*, 73: 1173-1181.
57. Guo, Y. and D.A. Rockstraw, 2007. Activated carbons prepared from rice hull by one-step phosphoric acid activation. *Micropor Mesopor Mater*, 100: 12-19.
58. Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J.O. Skjemstad, J. Thies, F.J. Luizao, J. Petersen and E.G. Neves, 2006. Black carbon increases cation exchange capacity in soils. *Soil Sci Soc Am J.*, 70: 1719-1730.
59. Cheng, C.H., J. Lehmann and M.H. Engelhard, 2008a. Natural oxidation of black carbon in soils: changes in molecular form and surface charge along a climosequence. *Geochim Cosmochim Acta.*, 72: 1598-1610.
60. Hammes, K. and M.W.I. Schmidt, 2009. Changes of biochar in soil. In Lehmann, J, Joseph S, (ed). *Biochar for environmental management: Science and technology*. 1st Ed., London: Earthscan, pp: 261-278.
61. Warnock, D., J. Lehmann, T. Kuyper and M. Rillig, 2007. Mycorrhizal responses to biochar in soil concepts and mechanisms. *Plant Soil*, 300: 9-20.
62. Pietikäinen, J., O. Kiikkilä and H. Fritze, 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus, *Oikos*, 89: 231-242.

63. Antal, M.J. and M. Gronli, 2003. The art, science and technology of charcoal production. *Industrial Engineering and Chemical Research*, 42: 1619-1640.
64. Waters, D., L. Van Zwieten, B. Pal Singh, A. Downie, L.C. Annette and J. Lehmann, 2011. Biochar in Soil for Climate Change Mitigation and Adaptation. Springer-Verlag Berlin Heidelberg, DOI: 10.1007/978-3-642-20256-8_15.
65. Jeffery, S., F.G.A. Verheijen, M. van der Velde, A.C. Bastos, 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric. Ecosyst. Environ.*, 144: 175-187.
66. Chan, K.Y., L. Van Zwieten, I. Meszaros, A. Downie and S. Joseph, 2008. Using poultry litter biochars as soil amendments. *Aust J Soil Res.*, 46: 437-444.
67. Biederman, L.A. and W.S. Harpole, 2013. Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy*, 5: 202-214.
68. Liu, X., A. Zhang, C. Ji, S. Joseph, R. Bian, L. Li, G. Pan and J. Paz-Ferreiro, 2013. Biochar's effect on crop productivity and the dependence on experimental conditions—A meta-analysis of literature data. *Plant Soil*. doi:10.1007/s11104-013-1806-x.
69. Hossain, M.K., V. Strezov, K.Y. Chan and P.F. Nelson, 2010. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere*, 78: 1167-1171.
70. Asai, H., B.K. Samson, H.M. Stephan, K. Songyikhangsuthor, K. Hommaa, Y. Kiyono, Y. Inoue, T. Shiraiwa and T. Horie, 2009. Biochar amendment techniques for upland rice production in Northern Laos. 1. Soil physical properties, leaf SPAD and grain yield. *Field Crops Research*, 111: 81-84.
71. IPCC, 2001. Climate Change: The Scientific Basis, Technical Summary by Workgroup I of the Intergovernmental Panel on Climatic Change, Cambridge, UK, Cambridge University Press.
72. IPCC, 2000. Land Use, Land-Use Change and Forestry, Watson RT, Noble R, Bolin B, Ravindranath NH, Verardo DJ, Dokken DJ (eds.), Intergovernmental Panel on Climatic Change Special Report, Cambridge, Cambridge University Press.
73. Izaurrealde, R.C., N.J. Rosenberg R. Lal, 2001. Mitigation of climate change by soil carbon sequestration, *Advances in Agronomy*, 70: 1-75.
74. Scholes, R.J. and I.R. Noble, 2001. Climate change storing carbon on land, *Science*, 294: 1012-1013.
75. Post, W.M. and K.C. Kwon, 2000. Soil carbon sequestration and land-use change: Processes and potential', *Global Change Biology*, 6: 317-328.
76. Freibauer, A., M.D.A. Rounsevell, P. Smith and J. Verhagen, 2004. Carbon sequestration in agricultural soils of Europe, *Geoderma*, 122: 1-23.
77. Lal, R., 2004. Agricultural activities and the global carbon cycle, *Nutrient Cycles in Agroecosystems*, 70: 103-116.
78. Seifritz, W., 1993. 'Should we store carbon in charcoal?', *International Journal of Hydrogen Energy*, 18: 405-407.
79. Sombroek, W., M.L. Ruivo, P.M. Fearnside, B. Glaser and J. Lehmann, 2003. Amazonian Dark Earths as carbon stores and sinks, in Lehmann J, Kern DC, Glaser B, Woods WI (eds.), *Amazonian Dark Earths: Origin, Properties, Management*, Dordrecht, Kluwer Academic Publishers, pp: 125-139.
80. Downie, A.E., L. Van Zwieten, R.J. Smernik, S. Morris and P.R. Munroe, 2011. Terra Preta Australis: Reassessing the carbon storage capacity of temperate soils. *Agriculture, Ecosystems & Environment*, 140(1-2): 137-147.
81. Sanborn, P., M. Geertsema, A.J. Timothy, Jull and B. Hawkes, 2006. Soil and sedimentary charcoal evidence for Holocene forest fires in an inland temperate rainforest, east-central British Columbia, Canada. *The Holocene*, 16(3): 415-427.
82. Day, D., R.J. Evans, J.W. Lee and D. Reicosky, 2005. Economical CO₂, SO_x and NO_x capture from fossil-fuel utilization with combined renewable hydrogen production and large-scale carbon sequestration, *Energy*, 30: 2558-2579.
83. Laird, D.A., R.C. Brown, J.E. Amonette and J. Lehmann, 2009. Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuels Bioprod Bioref*, 3: 547-562.